Stepwise Reduction of CaO and/or MgO Doped-Fe₂O₃ Compacts to Magnetite Then Subsequently to Iron at 1 173–1 473 K

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Compacts of pure Fe₂O₃ and Fe₂O₃-doped with either of 1.0% CaO and/or 1.0% MgO, sintered at 1 473 K for 20 h, were isothermally reduced at 1 173–1 473 K with 10%CO–90%CO₂ to magnetite then to metallic iron with purified CO. The oxygen weight-loss resulted from Fe₂O₃–Fe₃O₄ or Fe₃O₄–Fe reduction steps was continuously recorded as a function of time. Chemical and X-ray analyses, microscope examination and pore size analyzer were used to characterize the fired and reduced compacts. The influence of CaO and/or MgO on the reduction behaviour of Fe₂O₃ and Fe₃O₄ was intensively studied. The reduction mechanisms predicted from both of apparent activation energy values and heterogeneous gas–solid mathematical models were correlated with the microstructures of partially reduced samples. The results obtained showed that the doping of these fluxing oxides promoted the reduction of Fe₂O₃ at 1 173–1 473 K. The reduction of pure and doped Fe₂O₃ compacts is controlled by gaseous diffusion at early stages and by interfacial chemical reaction at later stages. In Fe₃O₄–Fe reduction step, the doping of CaO and/or MgO enhanced the reduction at early stages which is temperature and compact composition dependent. With progress in reduction, the presence of MgO retarded the reduction of Fe₃O₄ at ≤ 1 273 K resulting a slowing down in the rate at latter stages. This was attributed to formation of entrapped lower oxide relics which hindered gaseous diffusion. At early stages, the reduction of pure and doped Fe₃O₄ compacts is controlled by mixed control reaction mechanism. At latter stages, interfacial chemical reaction is the rate determining step for pure and CaO-containing samples, whereas solid-state diffusion is the rate controlling step for MgO-doped compacts.

KEY WORDS: gaseous reduction; carbon monoxide; hematite; magnetite; wustite; iron calciumferrite; magnesioferrite; calcium magnesium-ferrite.

1. Introduction

The reducibility of iron ores is an important parameter which has a great influence on the efficiency of an operating process. A detailed account and assessment of the work done prior to 1971 has been reviewed by Bogdandy and Engell.¹⁾ Despite the extensive research in this field, many questions still unanswered. This arising from the using of wide variety of starting materials having different physical and chemical nature and also from the several structural changes accompanying the reduction processes. The structure and properties of the intermediate solid products (magnetite and/or wustite) are important in heterogeneous gas–solid reactions, since the transport of the reducing gas to the reactant interface must proceed throughout these layers.²⁾

During the reduction of hematite (α -Fe₂O₃) into magnetite (Fe₃O₄), several changes of varying importance take place.³⁾ The morphology of the produced magnetite is greatly dependent on the reduction temperature and reducing gas composition.^{4–8)} The volume changes accompanying Fe₂O₃–Fe₃O₄ reduction step was found to increase by 8–12.5% (V/V).^{4,6,9)} The reduction of α -Fe₂O₃ at lower temperatures and higher

CO content leads to the formation of porous magnetite following a shrinking core reaction model. While at higher temperatures and low CO content, the reduction of hematite proceeded through formation of magnetite wedges (lamellae) in each grain and a dense magnetite is formed.^{4,10)} In the reduction model proposed by Edström¹¹⁾ and favoured by Thanning,¹²⁾ it has been considered that magnetite forms dense layer around hematite and thus separates it from the reducing gas. Further reduction is supposed to take place at the Fe₂O₃/Fe₃O₄ interface by the migrating of iron ions and electrons and the solid-state diffusion of ions is the rate determining step. Unal and Bradshaw⁹⁾ reported that the reduction of Fe₂O₃ to Fe₃O₄ with CO/CO₂ followed a shrinking core model at 873 K, whereas at 1 273 K, it followed a different path and proceeded by sideways thickening of finite number of magnetite lamellae. The influence of impurities such as oxides of Ca, Mg, Al or Si on the nucleation and grain growth of magnetite formed during the reduction of hematite was investigated by Chaigneau and Heerema.¹³⁾ They found that these oxides have different effects and formed as separate phase with Si, a solid solution within the iron oxide with Al, while a new mineralogical phase is formed with Ca and

Mg.

Among the reduction of magnetite, the earlier work by Edström¹⁴⁾ remain most noteworthy. Moran and Jenkins¹⁵⁾ concluded that the presence of trivalent ions that are soluble in wustite enhances the solid-state diffusion of Fe^{2+} ions and Fe. An extensive work by McKewan^{16–18)} indicated that, at low pressure, the reduction rate of Fe_3O_4 is directly proportional to the hydrogen partial pressure (P_{H_2}). While at higher pressure, the rate is linear function of (P_{H_2}) up to about 1 atm and above which the rate approaches a maximum limits. Quets *et al.*¹⁹⁾ found that the reduction of Fe_3O_4 to metallic iron is controlled by chemical reaction at the $\text{Fe}_3\text{O}_4/\text{Fe}$ interface below 843 K and above which a dense wustite (non porous) was formed over Fe_3O_4 surface. Rao and Al-Kahtany^{20–22)} investigated the reduction of Fe_3O_4 with H_2 and H_2 -containing gas mixtures. They observed the presence of consecutive stages in the reduction process namely; incubation, accelerating and decaying steps which were correlated with the nucleation and grain growth at the $\text{Fe}_3\text{O}_4/\text{Fe}$ interface.

On the light of the previous works,^{23,24)} it was found that the doping of CaO and/or MgO accelerated the reduction at early stages, while the doping of MgO retarded the reduction of Fe_2O_3 at latter stages. For better understanding the role of either CaO and/or MgO on the reduction of iron oxides, it is important to investigate their effect on each of the intermediate reduction steps. This investigation is undertaken to highlight their influence on the reduction kinetics and mechanism of Fe_2O_3 to Fe_3O_4 then from Fe_3O_4 to iron at 1173–1473 K.

2. Materials and Experimental Technique

Chemically pro-analysis powders ($> 74 \mu\text{m}$) of Fe_2O_3 , CaO and MgO were used in this investigation. About 1.85 g of Fe_2O_3 or Fe_3O_4 thoroughly mixed with either 1.0% CaO and/or 1.0% MgO (by weight) were pressed at 35 kN. The dried compacts ($d=8 \text{ mm}$ and $h=10 \text{ mm}$) were gradually fired at 1473 K for 20 h (7 K/min) in purified oxygen, then cooled down to room temperature. The preparation, firing and cooling of compacts were previously described.^{23,24)}

The reduction assembly and the gas flow system used were previously mentioned.²⁵⁾ At a given temperature (1173–1473 K), the reduction was carried out in two subsequent steps in which; hematite is first converted to magnetite in 10%CO–90%CO₂ gas mixture then to

metallic iron in pure CO. In each experiment, fired compact, placed in the middle zone of the reduction furnace, was gradually heated up to the predetermined temperature, then 1.75 l/min of 10%CO–90%CO₂ gas mixture is introduced and the oxygen weight-loss, resulted from Fe_2O_3 – Fe_3O_4 transformation step, was continuously recorded as a function of time. When the sample reached to its constant weight, CO\CO₂ was replaced by purified argon. After 5 min, 1.75 l/min of purified CO is introduced instead of argon and the oxygen weight-loss resulted from Fe_3O_4 –Fe reduction step was also recorded. The reduced compact was then cooled down in purified argon to room temperature. Preliminary tests indicated that 1.75 l/min gas flow rate is sufficient to overcome the gas boundary layer effect around the sample.

X-ray diffraction analysis, optical microscope, pore size analyser and chemical and carbon analyses were applied to characterise the fired and reduced compacts.

2.1. Characteristics of Fired Compacts

The physical characteristics and the different phases developed in the fired compacts are given in **Table 1**. It can be seen that while total porosity, pore diameter and pore volume developed in fired Fe_2O_3 compacts increased in CaO and/or MgO-doped compacts, the total pore area was decreased in MgO-containing samples. This resulted from the increase in the number of macropores formed between hematite grains on the expense of micropores inside these grains. The decrease in the total pore area in MgO-containing samples than in CaO– Fe_2O_3 compacts can be attributed to the difference in their internal structures.^{23,24)} During firing of compacts, CaO and/or MgO diffuses in Fe_2O_3 lattice forming calciumdiferrite (CF_2), magnesioferrite (MF) and calcium-magnesium-ferrate (C_2MF) phases. The photomicrographs showed the internal structure of the fired pure Fe_2O_3 , CaO– Fe_2O_3 , MgO– Fe_2O_3 and CaO/MgO– Fe_2O_3 compacts were previously given and discussed.^{23,24)} The different phases formed in fired samples were identified by X-ray analysis and also by subjecting the polished sections to different etching solutions.²⁶⁾ The structure developed in doped Fe_2O_3 compacts is characterised by the formation of central macropores in the vicinity of ferrite and ferrate phases.²⁷⁾

Table 1. Characteristics of pure and doped Fe_2O_3 compacts fired at 1473 K for 20 h in O₂ atmosphere.

Compact composition	Total porosity (%)	Total pore volume (cc/g)	Mean pore diameter (μm)	Total pore area (m^2/g)	Phases identified (XRD)
Pure Fe_2O_3	12.15	0.0070	0.312	0.953	$\alpha\text{-Fe}_2\text{O}_3$
1.0%CaO– Fe_2O_3	15.09	0.0215	8.545	1.606	$\alpha\text{-Fe}_2\text{O}_3$, CF_2
1.0%MgO– Fe_2O_3	16.31	0.0113	4.912	0.753	$\alpha\text{-Fe}_2\text{O}_3$, MF
CaO/MgO– Fe_2O_3	18.72	0.0120	6.085	0.794	$\alpha\text{-Fe}_2\text{O}_3$, CF_2 , MF, C_2MF

$\alpha\text{-Fe}_2\text{O}_3$ = Hematite

CF_2 = Calcium-diferrite phase ($\text{CaO} \cdot 2\text{Fe}_2\text{O}_3$)

MF = Magnesioferrite ($\text{MgO} \cdot \text{Fe}_2\text{O}_3$)

C_2MF = Calcium-magnesiumferrate ($2\text{CaO} \cdot \text{MgO} \cdot \text{Fe}_2\text{O}_3$)

3. Results and Discussion

Fired pure Fe_2O_3 and doped Fe_2O_3 compacts were isothermally stepwisely reduced to magnetite then to metallic iron at 1173–1473 K. At a given temperature, the indurated compacts were first, reduced to magnetite with 10%CO–90%CO₂, then subsequently to metallic iron with pure CO. In Fe_2O_3 – Fe_3O_4 and Fe_3O_4 –Fe reduction steps, the influence of doping oxide composition on the reduction of iron oxides was intensively investigated. The reduction kinetics were correlated with the microstructure of partially reduced samples. Moreover, different mathematical heterogeneous gas–solid reaction models were applied to predict the reduction mechanism.

3.1. Hematite–Magnetite Reduction Step

3.1.1. Reduction Behaviour

Compacts of pure Fe_2O_3 and Fe_2O_3 doped with either 1.0% CaO and/or 1.0% MgO were isothermally reduced at 50 K intervals between 1173 and 1473 K with 10%CO–90%CO₂ gas mixture to magnetite. The typical reduction curves obtained at 1173, 1223, 1273 and 1373 K are shown in Figs. 1(a), 1(b), 1(c) and 1(d) respectively. Generally, it can be observed that the presence of CaO and/or MgO promote the reduction of Fe_2O_3 . The magnitude of this promotion effect is greatly dependent on the compact composition, temperature and reduction extents. At early stages, the rate of reduction increased in the order $\text{CaO/MgO-Fe}_2\text{O}_3 > \text{MgO-Fe}_2\text{O}_3 > \text{CaO-Fe}_2\text{O}_3 > \text{Fe}_2\text{O}_3$. As reduction proceeds, a relatively decrease in the reduction rate of $\text{MgO-Fe}_2\text{O}_3$ than $\text{CaO-Fe}_2\text{O}_3$ compacts was observed. At ≥ 1373 K, the doping of these fluxing oxide(s) revealed less significant effects at the latter stages as shown in Fig. 1(d).

The promotion in reduction rate of Fe_2O_3 , at early stages, due to the doping of either CaO and/or MgO is attributed to the relatively increase in their original porosity, pore diameter and pore volume which facilitate gaseous diffusion. Moreover, the doping of CaO and/or MgO in such content (1.0% by weight) favour the disorder in the iron oxide lattice due to the intrusion of these foreign cations (Ca^{2+} and/or Mg^{2+}) resulting an

Fig. 1. Effect of doping of 1.0% CaO and/or 1.0% MgO on the reduction behaviour of Fe_2O_3 compacts with 10%CO–90%CO₂ gas mixture at: (a) 1173 K (b) 1223 K (c) 1273 K (d) 1373 K

increase in the number of active sites at which the reducing gas can easily adsorbed and consequently increases the rate of reduction.^{23,24,28–30)} The decrease in the rate of reduction in compacts doped with MgO than with CaO at intermediate stages, is attributed to the relatively lower reduction rate of magnesioferrite than calciumdiferrite.²⁴⁾ At latter stages, the higher reduction rate obtained in CaO/MgO– Fe_2O_3 than with MgO– Fe_2O_3 compacts is attributed to the relatively higher reduction rate of calcium-magnesiumferrite than hardly reducible magnesioferrite phase. The former phase was formed on the expense of the latter in the corresponding compacts.

3.1.2. Microscopic Examinations

Figures 2(a), 2(b), 2(c) and 2(d) showed the internal structures developed in 30% reduced Fe_2O_3 , CaO– Fe_2O_3 , MgO– Fe_2O_3 and CaO/MgO– Fe_2O_3 compacts at 1173 K respectively. It can be observed that magnetite is formed at the outermost surface of compacts followed by a more or less diffused interface between magnetite and the unreduced hematite. The structure of magnetite and the shape of interface are greatly dependent on the compact composition. In pure samples (Fig. 2(a)), a uniform structure of magnetite containing fine micropores is formed with a relatively sharp $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ interface. The structure given in Figs. 2(c) and 2(d) showed the formation of dense magnetite layer near the outer surface of compacts while porous magnetite is observed close to the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ interface. Unlike the

Fig. 2. Macrostructure of 30% reduced compacts with CO/CO₂ mixture at 1173 K. (a) Pure Fe_2O_3 (b) CaO– Fe_2O_3 (c) MgO– Fe_2O_3 (d) CaO/MgO– Fe_2O_3

structure observed in pure and MgO-containing samples, the structure developed in CaO-doped compacts (Fig. 2(b)), is characterised by the nucleation of magnetite along the internal boundaries of hematite grains in a more or less uniform pattern of growth. The microstructure of 85% reduced pure Fe_2O_3 , $\text{CaO-Fe}_2\text{O}_3$, $\text{MgO-Fe}_2\text{O}_3$ and $\text{CaO/MgO-Fe}_2\text{O}_3$ compacts developed at 1273 K can be seen in Figs. 3(a), 3(b), 3(c) and 3(d) respectively. The structure formed in CaO-doped compact (Fig. 3(b)) showed the nucleation and grain growth of dense magnetite layer along the internal boundaries of hematite grains. The magnetite nuclei is formed by the removal of oxygen from Fe_2O_3 lattice resulting a local variation in Fe/O ratio then transported from the points where oxygen was removed to the points where nucleation and growth occur. The produced magnetite grew as lamellae in some grains and with irregular patterns in others. The structure developed in 85% reduced $\text{MgO-Fe}_2\text{O}_3$ and $\text{CaO/MgO-Fe}_2\text{O}_3$ compacts (Figs. 3(c) and 3(d)) is characterised by the formation of $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ sharp interface and unreduced magnesioferrite patches partially entrapped in magnetite layer were also observed.

The photomicrographs showing the microstructure of completely reduced pure Fe_2O_3 , CaO , MgO and CaO/MgO -doped compacts with CO/CO_2 gas mixture to magnetite at 1273 K are given in Figs. 4(a), 4(b), 4(c) and 4(d) respectively. They showed that the shape and sizes of pores are greatly dependent on the compact composition. While large number of fine micropores are

formed in pure Fe_3O_4 compacts, different structures of macropores are developed in MgO-containing samples as shown in Figs. 4(c) and 4(d). In $\text{CaO-Fe}_3\text{O}_4$ compacts, Fig. 4(b), a relatively denser magnetite is formed in which large sizes of macropores can be distinguished between the grains. The increase in the number and volume of pores in magnetite compacts compared with that observed in the corresponding unreduced samples, is attributed to the removal of oxygen from the magnetite surface according to the model proposed by Unal and Bradshaw.⁹⁾ In this model iron ions and electrons associated with oxygen leave the surface of magnetite to $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ interface. The depressions on magnetite surface leads to further reactions and once a pore structure is formed, further oxygen remove will be limited resulting an increase in the pore volume. In doped Fe_3O_4 compacts, Ca^{2+} and/or Mg^{2+} ions diffuse in magnetite forming magnesioferrites and calcium-magnesioferrite which are distributed throughout the sample, while calcioferrite is formed as intergranular phase between magnetite grains in $\text{CaO-Fe}_3\text{O}_4$ compacts.

3.1.3. $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ Reduction Kinetics and Mechanism

The rate determining step in the reduction process can be predicted from both of apparent activation energy values, application of heterogeneous gas-solid reaction models and from the internal structure of partially reduced compacts.

Fig. 3. Microstructure of 85% reduced compacts with CO/CO_2 mixture at 1273 K.
(a) Pure Fe_2O_3 (b) $\text{CaO-Fe}_2\text{O}_3$
(c) $\text{MgO-Fe}_2\text{O}_3$ (d) $\text{CaO/MgO-Fe}_2\text{O}_3$

Fig. 4. Photomicrographs of magnetite formed at 1273 K with CO/CO_2 mixture.
(a) Pure Fe_3O_4 (b) $\text{CaO-Fe}_3\text{O}_4$
(c) $\text{MgO-Fe}_3\text{O}_4$ (d) $\text{CaO/MgO-Fe}_3\text{O}_4$

The apparent activation energy (E_a) is calculated from Arrhenius equation;

$$K_r = K_0 \cdot e^{-E_a/R_g \cdot T} \dots\dots\dots(1)$$

where K_0 is the frequency factor, R_g is the gas constant and T is the absolute temperature. The reaction rate constant (K_r) is derived from the relationship;

$$dr/dt = K_r \cdot p^n \dots\dots\dots(2)$$

where (p) is the reducing gas pressure and (n) is order of reaction. The Arrhenius plots in which the rate of reduction ($\log dr/dt$) at both initial and latter stages (5 and 85% extents) is plotted against ($1/T$) were made. From these plots, the computed values of apparent activation energy (E_a) obtained are given in **Table 2**. The values of (E_a) obtained, revealed that the reduction of pure and doped samples is controlled by gaseous diffusion mechanism at early stages and by interfacial chemical reaction at latter stages. The application of different heterogeneous gas-solid mathematical models indicated that the grain model derived by Szekely *et al.*³¹⁾ is the most reliable. In this model, they verified different mathematical formulae for gaseous diffusion, interfacial chemical reaction and mixed control reaction mechanisms. The simplified forms of these formulae are^{23,24)};

a- for gaseous diffusion;

$$p_{F_g}(X) = X + (1-X) \ln(1-X) = (2F_g F_p t^* / \sigma_g^2) = t^* / \sigma_g^2 = k_1 t \dots\dots\dots(3)$$

b- for chemical reaction;

$$g_{F_g}(X) = 1 - (1-X)^{1/F_g} = 1 - (1-X)^{1/2} = t^* = k_2 t \dots\dots\dots(4)$$

(for cylindrical compacts)

c- for mixed control reaction;

$$t^* = g_{F_g}(X) + \sigma_g^2 p_{F_g}(X), \text{ then;}$$

$$t^* = [1 - (1-X)^{1/2}] + \sigma_g^2 [X + (1-X) \ln(1-X)] = k_3 t \dots\dots\dots(5)$$

The generalized gas-solid reaction modulus (σ^2) can be calculated from:

$$\sigma_g^2 = (V_p/A_p)^2 \cdot [(1-\varepsilon)kC_{A0}^{-1}F_p]/2D_e \cdot (A_g/V_g F_g) \dots\dots(6)$$

Under Fe_2O_3 - Fe_3O_4 reduction conditions, the calculated value of the generalized gas-solid reaction modulus (σ_g^2) is $1 (\pm 0.05)$, accordingly Eq. (5) can be simplified into;

$$t^* = [1 - (1-X)^{1/2}] + [X + (1-X) \ln(1-X)] = k_3 t \dots\dots(7)$$

where;

Table 2. Apparent activation energy values (E_a) for the reduction of pure and doped Fe_2O_3 compacts at 1173–1473 K.

Compact composition	Apparent activation energy (kJ/mol)	
	at 5% extent	at 85% extent
Pure Fe_2O_3	20.69	60.09
1.0%CaO- Fe_2O_3	18.35	50.70
1.0%MgO- Fe_2O_3	17.84	66.46
CaO/MgO- Fe_2O_3	17.14	56.71

k_1, k_2, k_3 = constants (sec^{-1}),

F_g, F_p = shape factor for grains and compacts respectively (= 1, 2 and 3 for flat plates, cylinders and spheres respectively),

V_g, V_p = volume of individual grains and compacts respectively (cm^3),

A_g, A_p = external surface area of the individual grains and compacts (cm^2/g),

C_{A0} = gaseous-reactant concentration in the bulk ($\text{g mol}/\text{cm}^2$),

t^* = dimensionless time,

D_e = effective diffusivity of gaseous reactant in porous compact (cm^2/sec),

ε = total porosity of compact in %, and

σ = gas-solid reaction modulus, and

X = fractional reduction degree at a given reduction time (t) in sec.

The kinetic formulae given in Eqs. (3), (4) and (7) were tested against the experimental reduction results. A set of straight lines was only obtained on applying the gaseous diffusion formula at the early stages of reduction up to certain extents as shown in **Figs. 5(a), 5(b), 5(c)** and **5(d)** for pure Fe_2O_3 , CaO- Fe_2O_3 , MgO- Fe_2O_3 and CaO/MgO- Fe_2O_3 compacts respectively. Also it can be noticed that for a given compact composition, the extent of reduction at which the reduction is controlled by gaseous diffusion mechanism increased with rise in temperature. At > 50% reduction extents, the gaseous diffusion mechanism is no longer valid as the rate determining step since deviations from straight lines were observed. Accordingly, interfacial chemical reaction and mixed control formulae (Eqs. (4) and (7)) were tested. Straight lines were only obtained on applying the interfacial chemical reaction formula as shown in **Figs. 6(a), 6(b), 6(c)** and **6(d)** for pure Fe_2O_3 , CaO- Fe_2O_3 , MgO- Fe_2O_3 and CaO/MgO- Fe_2O_3 samples respectively. Thus, it can be concluded that the reduction of pure and doped hematite compacts to magnetite with CO/ CO_2 at 1173–1473 K is controlled by gaseous

Fig. 5. Application of mathematical gaseous diffusion control equation at early stages of reduction of compacts at 1173–1473 K.
(a) Pure Fe_2O_3 (b) CaO- Fe_2O_3
(c) MgO- Fe_2O_3 (d) CaO/MgO- Fe_2O_3

diffusion at early stages up to certain reduction extents then by interfacial chemical reaction till the final stages of reduction.

The influence of doping oxide composition on the internal structure of 30 and 85% reduced pure Fe_2O_3 and Fe_2O_3 doped samples were shown in Figs. 3 and 4 respectively. At early stages of reduction, dense magnetite is formed at the outermost surface of compacts followed by $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ diffused interface. The structure developed at early stages indicated that the reduction is most likely controlled by gaseous diffusion with negligible contribution of interfacial chemical reaction. The photomicrographs given in Fig. 4 for 85% reduced compacts, showed the formation sharp $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ interface between the produced magnetite and the un-reduced hematite layers following a shrinking core mode of reaction. The developed structure indicated that the interfacial chemical reaction has a pronounced effect as the rate controlling mechanism at the latter stages of reduction.

Therefore, the reduction mechanism elucidated from apparent activation energy values, application of gas-solid mathematical models and from the microstructure of partially reduced samples are in agreement with each other. They confirmed that the reduction of pure and doped- Fe_2O_3 compacts at 1173–1473 K to magnetite with CO/CO_2 is controlled by gaseous diffusion at early stages and by interfacial chemical reactions at latter stages. The gradual transformation from the former to the latter mechanism is greatly dependent on reduction temperature and compact composition.

Fig. 6. Application of mathematical interfacial chemical reaction control equation at latter stages of reduction of compacts at 1173–1473 K.

(a) Pure Fe_2O_3 (b) $\text{CaO}-\text{Fe}_2\text{O}_3$
(c) $\text{MgO}-\text{Fe}_2\text{O}_3$ (d) $\text{CaO}/\text{MgO}-\text{Fe}_2\text{O}_3$

3.2. Magnetite–Iron Reduction Step

At a given temperature (1173–1473 K), pure Fe_3O_4 and CaO and/or MgO -doped Fe_3O_4 compacts produced from the isothermal reduction of the corresponding hematite samples with CO/CO_2 gas mixture, were subsequently reduced with pure CO to metallic iron. The internal structure of pure Fe_3O_4 , $\text{CaO}-\text{Fe}_3\text{O}_4$, $\text{MgO}-\text{Fe}_3\text{O}_4$ and $\text{CaO}/\text{MgO}-\text{Fe}_3\text{O}_4$ samples formed at 1273 K were shown in Figs. 4(a), 4(b), 4(c) and 4(d) respectively while their characteristics are given in Table 3. It can be noticed the total porosity, pore volume and pore diameter developed in pure magnetite compacts increased due to the doping of CaO and/or MgO . This resulted from the formation of ferrite and ferrate phases which are characterized by the formation of central macropores.²⁷⁾ On the other hand, the decrease in the pore area in doped samples is resulted from the fluxing effect of CaO and/or MgO which enhance sintering and densification of magnetite grains. The relationship between the measured pore diameter and the cumulative pore volume in pure and doped magnetite compacts is shown in Fig. 7. It can be seen that the pore volume increased with the decrease in the pore diameter. Also the doping of CaO and/or MgO increases the pore volume giving a relatively higher values in CaO -doped compacts. In doped Fe_3O_4 compacts, calciumdiferrite (CF_2), magnesioferrite (MF) and calcium-magnesioferrite (C_2MF) phases were developed and identified by X-ray analysis technique.

3.2.1. Reduction Behaviour

The isothermal reduction curves obtained from the reduction of pure and doped magnetite compacts with CO at 1173, 1223, 1273 and 1373 K are shown in Figs. 8(a), 8(b), 8(c) and 8(d) respectively. It can be observed

Fig. 7. Influence of doping oxide composition on the structure of pores formed in magnetite compacts produced at 1273 K.

Table 3. Characteristics of pure and doped Fe_3O_4 compacts formed at 1273 K.

Compact composition	Total porosity (%)	Total pore volume (cc/g)	Mean pore diameter (μm)	Total pore area (m^2/g)	Phases identified (XRD)
Pure Fe_3O_4	16.97	0.015	2.232	4.377	Fe_3O_4
1.0% $\text{CaO}-\text{Fe}_3\text{O}_4$	19.85	0.035	12.124	2.856	Fe_3O_4 , CF_2
1.0% $\text{MgO}-\text{Fe}_3\text{O}_4$	18.95	0.029	7.459	2.685	Fe_3O_4 , MF
$\text{CaO}/\text{MgO}-\text{Fe}_3\text{O}_4$	19.10	0.032	9.254	2.795	Fe_3O_4 , CF_2 , MF, C_2MF

Fig. 8. Effect of CaO and/or MgO on the reduction behaviour of magnetite compacts with pure CO at:

(a) 1173 K (b) 1223 K (c) 1273 K (d) 1373 K

that the doping of either CaO and/or MgO revealed significant effects during the reduction of Fe₃O₄ at ≤ 1273 K. At initial stages, the doping of CaO and/or MgO promoted the reduction of Fe₃O₄ and the rate of reduction increased in the order MgO-Fe₃O₄ > CaO/MgO-Fe₃O₄ > CaO-Fe₃O₄ > Fe₃O₄. A gradual decrease in this promotion effect was observed with rise in temperature. At intermediate stages, the doping of MgO hindered the reduction of Fe₃O₄ resulting a slowing down in the rate at latter stages at ≤ 1273 K. The promotion effect at early stages is attributed to both of the increase in the original porosity and the disorder in iron oxide lattice due to the intrusion of these foreign cations. The slowing down in the rate of MgO-doped Fe₃O₄ compacts at latter stages is attributed to the increase in the number and sizes of the formed hardly reducible magnesiowustite relics. At lower temperatures, the presence of these relics hindered gaseous diffusion and consequently lowered the reduction rate of Fe₃O₄. The doping of CaO with MgO in Fe₃O₄ compacts eliminated this slowing down effect due to formation of relatively easier reducible calciowustite (CaO·FeO) and calcio-magnesiowustite (2CaO·MgO·FeO) phases. The latter phase was formed on the expense of hardly reducible magnesiowustite (MgO·FeO) phase. Sugiyama *et al.*³²⁾ pointed out that the doping of MgO improves the reducibility of iron oxides at 1523 K, but not at 1173 K. This is because the presence of MgO inhibits liquid slag formation during reduction which tends to fill the pores and to promote a slag layer formation around the iron oxides. At lower temperatures, there is no liquid formation, and the reducibility of magnesiowustite was lower than hematite. Therefore, the doping of MgO in the compacts was harmful at latter stages, when reduction is carried out at lower temperatures.

3.2.2. Microscopic Examinations

The photomicrographs showing the internal structure of 30% reduced pure Fe₃O₄, CaO-Fe₃O₄, MgO-Fe₃O₄ and CaO/MgO-Fe₃O₄ samples at 1173 K, where the doping of these oxides promoted the reduction of Fe₃O₄, are given in Figs. 9(a), 9(b), 9(c) and 9(d) respectively. In pure compact (Fig. 9(a)), metallic iron is formed as a small nuclei on the wustite surface (light grey). The microstructure of CaO-doped samples given in Fig. 9(b)

Fig. 9. Macrostructure of 30% reduced compacts with pure CO at 1173 K.

(a) Pure Fe₃O₄ (b) CaO-Fe₃O₄
(c) MgO-Fe₃O₄ (d) CaO/MgO-Fe₃O₄

shows the nucleation of metallic iron along the outer surface of compact in which iron nuclei is grown up in a needle form oriented towards the centre of compact. Also, diffused interface between metallic iron and lower oxides layer can be distinguished. The structure developed in 30% reduced MgO-containing compacts (Figs. 9(c) and 9(d)) showed the formation of small wustite grains that are partially nucleated with metallic iron. Magnesiowustite patches (dark grey) is also observed close to the outer surface of compact.

On the other hand, at latter stages of reduction, the doping of MgO retarded the reduction of Fe₃O₄ at ≤ 1273 K, and this retardation was eliminated at higher temperatures. Thus, the microstructure of 85% reduced MgO-Fe₃O₄ at 1223 K and at 1373 K was examined as shown in Figs. 10(a) and 10(b) respectively. The structure developed at 1223 K showed that wustite and magnesiowustite grains are completely surrounded by dense metallic iron layer resulting completely entrapped relics as shown in Fig. 10(a). Under these conditions, the gaseous diffusion to the lower oxide surface is hindered and the solid-state diffusion of anions and cations has a pronounced effect in the reduction at ≤ 1273 K. At 1373 K, the structure given in Fig. 10(b) showed the decrease in the number and sizes of these entrapped lower oxide relics indicating that the contribution of solid-state diffusion in the reduction mechanism decreased with rise in temperature. Although the rise in temperature increases the ability of iron coatings and sinters around

Fig. 10. Microstructure of 85% reduced MgO-Fe₃O₄ compacts with pure CO at: (a) 1223 K (b) 1373 K

Table 4. Apparent activation energy values (E_a) for the reduction of pure and doped Fe₃O₄ compacts at 1173–1473 K.

Compact composition	Apparent activation energy (kJ/mol)	
	at 5% extent	at 85% extent
Pure Fe ₃ O ₄	32.35	72.47
1.0%CaO-Fe ₃ O ₄	25.92	54.28
1.0%MgO-Fe ₃ O ₄	28.01	126.49
CaO/MgO-Fe ₃ O ₄	27.17	67.92

the lower oxide relics, a matter which would decrease the rate of reduction, it must be emphasized that the mobility and migration of holes and cations (solid-state diffusion) are also favoured with rise in temperature. This in turn, promoted the reduction rate of Fe₃O₄ at higher temperatures.

3.2.3. Fe₃O₄-Fe Reduction Kinetics and Mechanism

The experimental results obtained from the reduction of pure and doped-Fe₃O₄ compacts with CO to metallic iron at 1173–1473 K were used to calculate the values of apparent activation energy. Moreover different heterogeneous gas-solid reaction formula were tested and correlated with the microstructure of reduced samples to elucidate the corresponding reduction mechanism.

For a given compact composition, the relationship between the rate of reduction ($\log dr/dt$) and the corresponding values of ($1/T$) at 5 and 85% reduction extents were plotted and the computed values of apparent activation energy (E_a) obtained are given in Table 4. At the early stages (5% extents), the values of (E_a) obtained revealed that the reduction of pure and doped Fe₃O₄ compacts is controlled by a combined effect of gaseous diffusion and interfacial chemical reaction mechanism. The contribution of the latter in the reduction mechanism decreased in the presence of these doping oxides. At the latter stages (85% extents), the interfacial chemical reaction is the rate determining step in the reduction of pure and CaO-containing compacts, while solid state diffusion is the rate controlling mechanism in the reduction of

Fig. 11. Application of mathematical mixed control equation at initial stages of reduction of compacts with CO at 1173–1473 K.

(a) Pure Fe₃O₄ (b) CaO-Fe₃O₄
(c) MgO-Fe₃O₄ (d) CaO/MgO-Fe₃O₄

MgO-Fe₃O₄ compacts.

In order to confirm the validity of reduction mechanisms elucidated from apparent activation energy values, heterogeneous gas-solid mathematical formulae for gaseous diffusion, interfacial chemical and mixed control reactions (Eqs. (3), (4) and (5)) were tested against the experimental results. Under the Fe₃O₄-Fe reduction conditions, the generalized gas-solid reaction modulus (σ_g^2) was calculated from Eq. (6) and its value was equal to 1.31 resulting a relatively higher contribution of gaseous diffusion in the mixed control mechanism. Consequently, the mixed control formula (Eq. (5)) is modified into;

$$t^* = [1 - (1 - X)^{1/2}] + 1.31 [X + (1 - X) \ln(1 - X)] \\ = k_3 t \quad \dots \dots \dots (8)$$

The testing of Eqs. (3), (4) and (8) against the experimental results obtained showed that straight lines were only obtained on applying the mixed control formula (Eq. (8)) at early stages up to certain reduction extents depending on temperature, as shown in Figs. 11(a), 11(b), 11(c) and 11(d) for pure Fe₃O₄, CaO-Fe₃O₄, MgO-Fe₃O₄, CaO/MgO-Fe₃O₄ respectively. This indicated that the reduction of pure and doped Fe₃O₄ compacts at 1173–1473 K is controlled by mixed control mechanism at their early stages of reduction. At $\geq 60\%$ extents, the reduction of pure Fe₃O₄, CaO-Fe₃O₄, Ca/MgO-Fe₃O₄ compacts is controlled by interfacial chemical reaction mechanism as shown in Figs. 12(a), 12(b) and 12(d) respectively. For MgO-doped compacts (Fig. 12(c)), straight lines were only obtained on applying the interfacial chemical reaction formula at ≥ 1373 K, whereas below which, none of the applied mathematical formulae were able to produce straight lines till the end of reduction process. This clearly indicated that, solid-state diffusion of anions (O^{2-}) and/or cations (Fe^{2+}) had a major contribution in the reduction of MgO-Fe₃O₄ at such lower temperatures.

The internal structure of 30% reduced samples given

Fig. 12. Application of mathematical interfacial chemical reaction control equation at latter stages of reduction of compacts with CO at 1173–1473 K.

(a) Pure Fe_3O_4 (b) $\text{CaO-Fe}_3\text{O}_4$
(c) $\text{MgO-Fe}_3\text{O}_4$ (d) $\text{CaO/MgO-Fe}_3\text{O}_4$

in Figs. 9(a)–9(d) showed the formation of diffused reaction interfaces. This indicated that the reduction of pure and doped compacts is controlled by a combined effect of gaseous diffusion and interfacial chemical reactions (mixed control mechanism). At latter stages, the microstructure of 85% reduced pure Fe_3O_4 and $\text{CaO-Fe}_3\text{O}_4$ compacts showed the development of sharp interfaces between the lower oxides and metallic iron layer. Under these conditions, the reduction of these compacts is controlled by interfacial chemical reaction mechanism. While, on the other hand, the structure developed in 85% reduced $\text{MgO-Fe}_3\text{O}_4$ compacts at ≤ 1273 K, showed the presence of completely entrapped relics in which dense metallic iron is nucleated along the whole surface of lower oxides grains as shown in Fig. 10(a). Accordingly, gaseous diffusion is hindered and the reduction is controlled by solid-state diffusion mechanism. At higher temperatures, the rate of solid state-diffusion and consequently the rate of reduction increases and the retardation in the reduction rate was eliminated due the decrease in the sizes and numbers of partially entrapped lower oxide relics as shown in Fig. 10(b).

From the applications of Arrhenius equation and gas-solid mathematical formulae and correlated with the microstructure of partially reduced samples, it can be concluded that the reduction of Fe_3O_4 and Fe_3O_4 -doped compacts at 1173–1473 K to metallic iron is controlled by mixed control mechanism at early stages. While, at latter stages, the reduction mechanism is temperature and compact composition dependent. The reduction of pure Fe_3O_4 and Fe_3O_4 doped with CaO or with CaO/MgO mixture is controlled by interfacial chemical reaction mechanism. For MgO -doped compacts, solid-state diffusion is the rate determining step at ≤ 1273 K, while interfacial chemical reaction mechanism is the rate controlling step at high temperatures.

4. Conclusion

Sintered compacts of pure Fe_2O_3 and Fe_2O_3 doped

with either 1.0% CaO and/or 1.0% MgO were isothermally reduced at 1173–1473 K. At a given temperature, compacts were first reduced with 10% CO –90% CO_2 gas mixture to magnetite then subsequently reduced with CO to metallic iron. The influence of doping oxide composition on the reduction kinetics and mechanism was intensively studied. The reduction mechanism was elucidated from activation energy values, application of gas-solid mathematical model and correlated with the internal structures of partially reduced samples. The results obtained revealed the followings;

(1) In Fe_2O_3 – Fe_3O_4 reduction step, the doping of either CaO and/or MgO promoted the reduction rate of Fe_2O_3 at 1173–1473 K. The magnitude of this promotion is temperature and extent of reduction dependent. At a given temperature, the reduction rate increased in the order $\text{CaO/MgO-Fe}_2\text{O}_3 > \text{MgO-Fe}_2\text{O}_3 > \text{CaO-Fe}_2\text{O}_3 > \text{Fe}_2\text{O}_3$. The promotion effect decreased with rise in temperature and increased with the increase in the reduction extents. The reduction of pure and doped compacts was controlled by gaseous diffusion mechanism at early stages and by interfacial chemical reaction mechanism at latter stages.

(2) In Fe_3O_4 – Fe reduction step, the doping of either CaO and/or MgO enhanced the reduction of Fe_3O_4 at early stages and this effect decreased with rise in temperature. At intermediate stages, the doping of compacts with MgO retarded the reduction of Fe_3O_4 at ≤ 1273 K resulting a slowing down in the rate at the latter stages. This was attributed to the formation of completely entrapped lower oxide relics which hindered gaseous diffusion to and from the lower oxide grains. The doping of CaO with MgO in Fe_3O_4 compacts eliminated the slowing down effect due to the development of relatively easier reducible calcio-magnesiowustite on expense of hardly reducible magnesiowustite phase. The reduction of pure and doped Fe_3O_4 compacts was controlled with mixed control reaction mechanism at their early stages. With reduction progress, the contribution of interfacial chemical reaction in the overall reduction mechanism increased till it became the rate determining step at latter stages for pure and CaO -containing Fe_3O_4 samples. While solid state diffusion is the rate controlling step for MgO -doped compacts at ≤ 1273 K.

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REFERENCES

- 1) L. Von Bogdandy and H. J. Engell: The Reduction of Iron Ores, Springer Verlag, Berlin, (1971).
- 2) A. V. Bradshaw: *Trans. Inst. Min. Metall.*, **79C** (1970), 281.
- 3) H. D. Megaw: *Crystal Structures: A Working Approach*, Saunders, Philadelphia, (1973).
- 4) A. V. Bradshaw and A. G. Matyas: *Metall. Trans.*, **7B** (1976), 81.
- 5) P. R. Swann and N. J. Tighe: *Metall. Trans.*, **8B** (1977), 479.
- 6) P. C. Hayes and P. Grieveson: *Metall. Trans.*, **12B** (1981), 579.
- 7) P. Baguley, D. H. St. John and P. C. Hayes: *Metall. Trans.*, **14B**

- (1983), 513.
- 8) M. Et-Tabirou, B. Dupre and C. Gleitzer: *Metall. Trans.*, **19B** (1988), 311.
- 9) A. Unal and A. V. Bradshaw: *Metall. Trans.*, **14B** (1983), 743.
- 10) A. G. Matyas and A. V. Bradshaw: *Ironmaking Steelmaking*, **1** (1974), 180.
- 11) J. O. Edström: *Jernkontorets Ann.*, **141** (1957), 809.
- 12) G. Thaning: *Jernkontorets Ann.*, **151** (1971), 47.
- 13) R. Chaigneau and R. H. Heerema: *Metall. Trans.*, **22B** (1991), 503.
- 14) J. O. Edström: *J. Iron Steel Inst.*, **175** (1953), 289.
- 15) V. J. Moran and A. E. Jenkins: *J. Iron Steel Inst.*, **199** (1961), 26.
- 16) W. M. McKewan: *Trans. AIME*, **212** (1958), 791.
- 17) W. M. McKewan: *Trans. AIME*, **218** (1960), 2.
- 18) W. M. McKewan: *Steelmaking: The Chipman Conf.*, ed. by J. F. Elliott, MIT Press, Cambridge, Mass., (1965), 139.
- 19) J. M. Quets, M. E. Wadsworth and J. R. Lewis: *Trans. AIME*, **221** (1961), 1186.
- 20) M. M. Al-Kahtany and Y. K. Rao: *Ironmaking Steelmaking*, **7** (1980), No. 2, 49.
- 21) Y. K. Roa and M. M. Al-Kahtany: *Ironmaking Steelmaking*, **11** (1984), No. 1, 34.
- 22) Y. K. Roa and M. M. Al-Kahtany: *Ironmaking Steelmaking*, **11** (1984), No. 2, 88.
- 23) A. A. El-Geassy: *ISIJ Int.*, **36** (1996), No. 11, 1328.
- 24) A. A. El-Geassy: *ISIJ Int.*, **36** (1996), No. 11, 1344.
- 25) S. Du, N. S. Srinivasan and L. I. Staffanson: *Scand. J. Metall.*, **17** (1988), 220.
- 26) K. Sanbongi, Y. Omori, T. Ikeno, S. Watanabe and N. Nishida: *Trans. Iron Steel Inst. Jpn.*, **7** (1967), 126.
- 27) M. Paulus and P. Y. Evans: *Reactivity of Solids*, John Wiley, NY, (1969), 585.
- 28) F. F. Vol'kenshtein: *Zh. Fiz. Khim.*, **22** (1948), 311.
- 29) S. E. Kalafalla and P. L. Weston: *Trans. AIME*, **239** (1967), 1494.
- 30) A. A. El-Geassy, K. A. Shehata and S. Y. Ezz: *Iron Steel Int.*, **49** (1976), 427.
- 31) J. Szekely, J. W. Evens and H. Y. Sohn: *Gas-Solid Reactions*, Academic Press, NY, (1967), 129.
- 32) T. Sugiyama, S. Shiroushi, O. Tsuchiya, M. Onoda and I. Fujita: *Trans. Iron Steel Inst. Jpn.*, **23** (1983), 153.